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(CORROSION OF TYPE 316 STAINLESS STEEL IN NaK SERVICE--
A LITERATURE SURVEY)

C. A. Zimmerman

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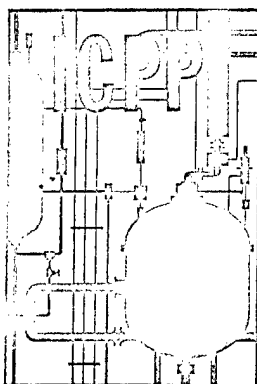
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CORROSION OF TYPE 316 STAINLESS STEEL IN NaK SERVICE - -
A LITERATURE SURVEY

by

C. A. Zimmerman

PHILLIPS
PETROLEUM
COMPANY



Atomic Energy Division
Contract AT(10-1)-205
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U. S. ATOMIC ENERGY COMMISSION

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A B S T R A C T

[A literature survey of work on corrosion of stainless steel, especially Type 316, by NaK and sodium has been made, based on information available through September, 1964. In general, the Type 316 and Type 304 stainless steels should give good performance with NaK. The mechanisms which can lead to failure are attack by impurities at temperatures under 550°C, and carbide precipitation, sigma formation, and mass transfer at higher temperatures.]

end

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CORROSION OF TYPE 316 STAINLESS STEEL IN NaK SERVICE - -
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I. SUMMARY

[Stainless steel Type 316 is the material of construction for the NaK heat exchange system in the Waste Calcining Facility at the Idaho Chemical Processing Plant. Concurrent with the use of this system, a survey of the recent literature has been completed regarding the performance of this metal in NaK service, and regarding the corrosion failures which might be possible. Information on corrosion reactions and mechanisms in NaK systems is not extensive due to limited use of this liquid metal. Therefore, it has been necessary to rely, to a large extent, on literature describing reactions of liquid sodium^{8,5}. A similarity exists between the performance of stainless steels in NaK and sodium, since oxygen is directly or indirectly associated with most of the mechanisms of corrosion and sodium monoxide has been demonstrated to be the insoluble oxide at equilibrium in NaK systems⁽²⁵⁾ containing up to 99.8 percent potassium.

The carburization of a Type 347 stainless steel has been reported in a sodium system where the only source of carbon was that contained in the sodium⁽⁵⁾. [The solubility of carbon in sodium is dependent upon oxygen content as well as upon temperature⁽¹⁴⁾, thus the concentration of oxygen in the system exerts a direct influence on carburization and decarburization reactions.

Nitriding of container materials including stainless steels has been reported in sodium systems containing nitrogen in the cover gas^(6,13). [Nitrogen build-up has been reported in one case in a sodium system under helium where no leaks in the system were detected⁽⁹⁾. [The solubility of nitrogen is increased by the presence of calcium in the liquid metal system. The synergistic action of nitrogen and oxygen together in the circulating liquid metal appears to be a potential source of accelerated corrosion.

Sensitization, sigma formation, and mass transfer are mechanisms which are promoted by elevated temperatures -- generally above 550°C. Serious corrosion by these mechanisms is generally controlled by proper selection of materials, equipment design, and operating procedures.

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II. INTRODUCTION

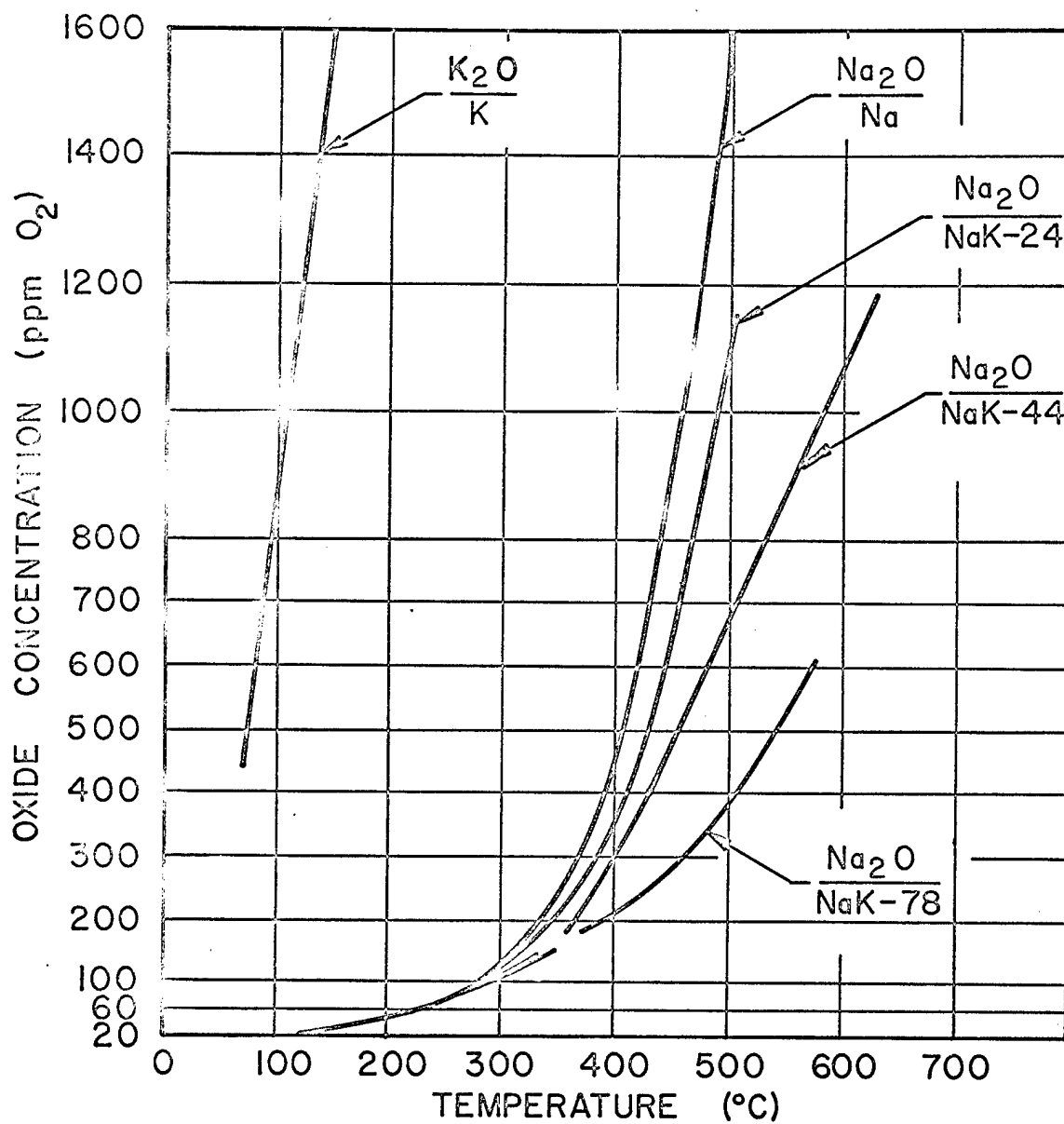
The Waste Calcining Facility (WCF) at the Idaho Chemical Processing Plant is operated to convert radioactive solvent extraction raffinates containing aluminum nitrate, acids, and other salts, to chemically stable salts or oxides. The calcination is accomplished in a fluidized bed which is heated by circulating NaK in a tube bundle in the bed. Although the use of liquid metals for heat transfer service is quite common, and corrosion failures were not anticipated, it has been advisable to review and summarize the pertinent literature data on the performance of stainless steel Type 316, which is used extensively in the heat transfer loop.

Information concerning NaK heat exchange systems is not plentiful; therefore, it has been necessary to use data describing sodium systems in this survey. Oxygen, in the form of sodium monoxide, appears to contribute either directly or indirectly to most of the mechanisms of corrosion observed in NaK systems. Burdi⁽⁷⁾ reports that the oxide precipitating from NaK at 200°C is entirely sodium monoxide and Williams, et al⁽²⁵⁾, note that the insoluble oxide at equilibrium in most NaK systems is sodium monoxide. Therefore, the use of corrosion data from sodium heat exchange systems to indicate mechanisms of corrosion attack of NaK heat exchange systems is believed to be valid.

785°C — The WCF heat exchange system is constructed of welded Type 316 stainless steel (part of which is columbium stabilized) and uses a eutectic of NaK as the circulating fluid. This eutectic is composed of 22 percent sodium and 78 percent potassium (freezing point about -13°C, boiling point about ~~894~~ 894°C) and has a density of ~ 0.85 g/cc at 100°C. The system operates at a maximum temperature of 760°C and a minimum of 110°C. Under normal operating conditions the temperature varies between 750°C and 570°C in the main circulating system. The system is helium blanketed and maintained under a pressure of 4 psig. A side stream "cold-trap", which is operated at 120°C, should reduce the oxygen content to ~ 20 ppm in this side stream^(3,24) according to the data shown in Figure 1. In actual practice, the total NaK system usually operates in the 30-50 ppm oxygen range.

III. CORROSION ASSOCIATED WITH CHEMICAL CONTAMINANTS

The austenitic stainless steels do not undergo direct reaction with pure molten sodium at temperatures below 650°C⁽¹⁰⁾. Corrosion is a function of temperature, impurity, and impurity concentration. The normally gaseous elements -- oxygen, hydrogen, and nitrogen -- along with carbon are impurities demonstrating the greatest influence on corrosion. Bruggeman⁽⁴⁾ has shown that metallic impurities in commercial sodium are present in amounts so small that they offer no corrosion problem.



CPP-S-3364

Fig. 1 Oxide Solubilities

1. Oxygen

Oxygen is the most important impurity in the liquid sodium corrosion system. Although the exact role of oxygen is unknown, the presence of oxygen in appreciable amounts (above 100 ppm) increases the total amount of corrosion, accelerates intergranular penetration, and is responsible for excessive mass transfer⁽¹⁾.

Wide experience in several laboratories has shown that austenitic Types 304 and 347 stainless steels do not oxidize appreciably in sodium containing less than 100 ppm oxygen at temperatures below 650°C⁽¹⁰⁾.

LaQue and Copson⁽¹⁷⁾ state that if the oxygen content exceeds about 200 ppm, the corrosion rate of stainless steels increases markedly. Above about 1000 ppm oxygen, they report that sodium oxide will attack stainless steels intergranularly and form a brittle surface layer.

The results of loop tests reported by Perlow and Page⁽²⁰⁾ using NaK containing less than 20 ppm oxygen in different containment materials, one of which was Type 316 stainless steel, led them to conclude that: "It is impossible to establish a realistic specification on the maximum amount of oxygen tolerable in sodium or NaK utilized as a coolant for a high temperature reactor. -- In general, however, oxygen contamination of the coolant to a reasonable level appears to lose significance above 650°C."

Detailed results of work reported by Perlow⁽¹⁹⁾ are presented in Tables I and II. The data demonstrate that there is no significant change in corrosion attack of stainless steels 304, 316 and 347 exposed at 650°C or 760°C in NaK-78 containing less than 20 ppm oxygen.

Mausteller⁽¹⁸⁾ reports the results presented in Table III, which point out that the preferential leaching rate of different alloy components from Type 347 stainless steel varies with oxygen content in a sodium system at 495°C.

Weeks⁽²⁴⁾, in his discussion of liquid metal corrosion mechanisms, states that oxygen in the alkali metals may have either or both of two effects: it may accelerate corrosion by catalyzing dissolution of the solid metal atoms, or oxygen itself may be the major migrating constituent.

A mechanism for oxygen-catalyzed mass transfer is presented schematically as:



FeO is presumed to be soluble as $(\text{Na}_2\text{O})_2 \cdot \text{FeO}$

∴ corrosion rate can be written as

$$\frac{d(\text{FeO})}{dt} = k_A (\text{Na}_2\text{O})$$

Table I

CORROSION DATA FOR NaK-78 SYSTEMS AT 650°C

Card 3/4

60930

<u>Type of Stainless Steel</u>	<u>Duration (hr)</u>	<u>Type and Depth of Attack</u>
304	1500	No apparent attack
	2500	1.4 mil intergranular corrosion
	3500	Evidence of general corrosion
	4500	1.5 mil pitting
316(a)	1000	2.6 mil general corrosion
	2000	2.5 mil intergranular corrosion
	3000	1.0 mil general corrosion
347	1500	0.7 mil intergranular corrosion ^(b)
	2500	2.0 mil general corrosion
	3500	1.9 mil intergranular corrosion
	4500	2.0 mil pitting

(a) These high corrosion rates due to unknown, excess oxygen in loop; results were not considered realistic by the author. They are included here to illustrate the extent and nature of the attack under these conditions.

(b) Grain boundary decarburization to a depth at 4.6 mils and massive carbides were observed.

Table II

CORROSION DATA FOR NaK-78 SYSTEMS AT 760°C

Card	Type of	Duration	Type and Depth of Attack
	<u>Stainless Steel</u>		
60930	304	1500	No apparent attack, slight evidence of decarburization
		2500	1.4 mil pitting
		3500	1.3 mil intergranular corrosion
		4500	2.3 mil decarburization
	316	1000	Slight evidence of general corrosion
		2000	0.4 mil decarburization
		3000	0.8 mil decarburization
	347	1500	0.6 mil intergranular corrosion ^(a)
		2500	0.4 mil pitting
		3500	General corrosion to a depth of 0.6 mil
		4500	2.5 mil decarburization

(a) With massive carbides and no evidence of grain growth.

Table III

EFFECT OF OXYGEN CONTENT ON PREFERENTIAL
LEACHING OF COMPONENTS FROM TYPE 347 STAINLESS STEEL

Element Leached	Leaching Rate, $\text{mg}/(\text{cm}^2)(\text{mo})$	
	30 ppm Oxygen	100 ppm Oxygen
Fe	2.5	40
Co	0.2	1
Ta	1.0	4
Mn	7.2	26

The reaction is presumed to reverse in the colder portion of the flowing system. The predicted first order dependence has been experimentally demonstrated. Oxygen-catalyzed mass transfer through sodium was observed at KAPL with nickel, chromium, cobalt, manganese, and tantalum from stainless steels; however, J. DeVan⁽²⁴⁾ has found nickel to be less sensitive than the other metals to oxygen-catalyzed mass transfer; perhaps as a result of the higher solubility of nickel.

When the oxide of a solid metal is insoluble in the liquid metal, oxygen exchange is observed; oxygen from the alkali metal reacts with the solid metal surface, where it either forms surface oxides or dissolves in/and embrittles the solid metal. Alternately, oxygen in the solid metal may be leached out by the liquid metal, resulting in severe intergranular attack.

Results of Perlow and Page⁽²⁰⁾ in the loop tests referred to previously (NaK containing less than 20 ppm oxygen at periods of up to seven months) indicate that Type 316 stainless steel had undetectable thickness change and a corrosion affected zone less than three mils deep. Metallographic examination revealed carbide precipitation, but not intergranular attack, when the exposure was continuous. When the exposure period was interrupted for observations, both carbide precipitation and intergranular attack were observed.

The oxygen content of a circulating sodium or NaK heat transfer stream can be controlled by either of two methods: the first involves the low temperature removal (cold-trapping) of Na_2O (the only oxide that is of significance in sodium or NaK alloys)⁽²⁵⁾ from the system by precipitation or crystallization. If the temperature of the alkali metal stream is decreased to less than 150°C , the oxygen content of that stream should be reduced below 50 ppm^(3,25) as shown in Figure 1. The second method of removing oxygen from a flowing alkali metal system is by using a getter (ie, materials such as barium, calcium, magnesium, zirconium,

and others that will preferentially remove oxygen from the flowing alkali metal system). Removal of oxygen by this method is done at elevated temperatures in order to influence reaction rate and is referred to as "hot-trapping".

2. Carbon

Wide experience in several laboratories has shown that austenitic Types 304 and 347 stainless steels in sodium systems containing less than 100 ppm oxygen and at temperatures below 650°C will react with carbon to form carburized layers, the depths of which are dependent on time and temperature of contact. Below 550°C this phenomenon is of minor importance⁽¹⁰⁾. Carlander and Hoffman⁽⁸⁾ cite previous work⁽¹¹⁾ leading to the statement that the extent to which carbon is transferred between dissimilar metals in contact with molten sodium depends not only upon the original carbon contents of the metals, but upon the oxygen content of the sodium. Sinizer and Pearson⁽²²⁾ report that the effect of oxygen content on the carburizing potential of molten sodium is unknown, but there are indications that the effect is not significant at oxygen levels below about 50 ppm.

Shephard⁽²¹⁾ cites several reported occurrences of carburization of Types 304 and 347 stainless steels in sodium service at temperatures below 650°C, and cautions that: "Stainless steel components with a brittle carburized surface are to be avoided because surface cracks are likely to form where the metal yields to relieve high stresses. Once formed, cracks propagate with relatively small repeated stresses and unexpected failures may result".

The carburization of Type 316 stainless steel in sodium saturated with carbon at 650°C has been reported⁽²⁸⁾; hardened case depths of 0.8, 1.4, and 2.7 mils were experienced over exposure periods 2, 7, and 16 days. It is also noted that grain boundary carbide precipitation is evident to a depth approximately twice as great as in the heavy carburized case. These results obtained by exposure of stainless steel tabs (Types 304 and 316) to 650°C sodium are very similar to those reported by Anderson and Sneesby⁽²⁾ on Type 304 stainless steel in terms of case depth as a function of time.

Gratton⁽¹⁴⁾ presents information showing the relationship between the solubility of carbon and time for dissolution in sodium containing 40 ppm oxygen at 500°C. This information is reproduced in Table IV. It is interesting to note that a carbon equilibrium under these conditions is reached in the relatively short time of only eight hours. The effect of oxygen concentration upon the solubility of carbon in sodium at various temperatures is also reported by Gratton. This information is summarized in Table V. These data demonstrate that increasing temperature or oxygen content will increase the amount of carbon soluble in sodium.

Table IV

DISSOLUTION RATE OF CARBON IN SODIUM CONTAINING
40 ppm OXYGEN AT $500 \pm 2^\circ\text{C}$

<u>Time, Hrs</u>	<u>Carbon Concentration (ppm)</u>
$\frac{1}{2}$	19
1	43
2	48
4	51
8	68
24	62
48	69
72	63

Table V

EFFECT OF TEMPERATURE AND OXYGEN CONTENT UPON THE
SOLUBILITY OF CARBON IN SODIUM^(a, b)

<u>Oxygen Content of Sodium</u>	<u>Carbon Solubility</u>			
(ppm)				
	147°C	300°C	500°C	700°C
40	32	48	65	74
260	113	136	171	185

(a) It is assumed that equilibrium conditions existed.

(b) These results are the experimental averages of several determinations.

Brush⁽⁵⁾ has reported the carburization of Type 347 stainless steel to a depth of 3.7 mils in the ALPALUS sodium heat transfer system at 455°C. There was no apparent source of carbon in this system other than that present in the original sodium.

Tests reported by Anderson and Sneesby⁽²⁾ show the carbon content of commercial grades of sodium to be approximately 60 ppm. They state that commercial grades of sodium cause carburization of Type 304 stainless steel, indicating that the carbon content of sodium in equilibrium with as-received Type 304 stainless steel is less than the carbon content of commercial sodium. This reference concludes that sodium containing 15 to 18 ppm carbon is in virtual equilibrium with uncarburized Type 304 stainless steel at 650°C, when the oxygen concentration in the sodium is less than 40 ppm.

Shephard⁽²¹⁾ reports that, the carbon in austenitic steels tends to form a chromium carbide precipitate at the grain boundaries when heated in the temperature range 430-815°C. Such a steel is "sensitized" and will be subject to intergranular corrosion in aqueous corrosive solutions. Sensitization does not appear to affect the corrosion resistance of the steel to liquid sodium, and intergranular attack of Type 304 stainless steel has not been encountered in low-oxygen sodium at temperatures up to 595°C.

Ferguson⁽¹²⁾ reports that stainless steel alloys such as Types 304 and 316 have been found to resist attack in sodium regardless of their structural condition. As a result of 595°C exposure in sodium, Types 304 and 316 stainless steels became "sensitized", that is, original carbide precipitated as very fine particles at grain boundaries and along crystallographic planes within grains that were in a stressed condition. Ferguson states that sensitized stainless steel is very susceptible to attack by any medium that is corrosive; however, sensitized Types 316 and 304 welds were not attacked by sodium. So long as stainless steel contacts only sodium, carbon pick-up or precipitation due to "sensitization" has no effect on its corrosion resistance. However, if the stainless steel in this condition should come in contact with aqueous reagents, there is a great possibility it would be subject to intergranular attack and perhaps final failure.

In discussing the mechanism of the carburization of stainless steel in sodium, Shephard⁽²¹⁾ reports that the carburization takes place mainly by grain boundary diffusion in the 400-540°C temperature range, while at 650°C and above volume diffusion predominates.

Grain boundary diffusion produces carburization mainly at the grain boundaries, resulting in an undesirable structure. Mechanical tests have not been made on stainless steel which has been subjected to the low-temperature, grain boundary diffusion type of carburization. Surface cracks that are produced by bending indicate that the surface of this material is brittle at room temperature.

Volume diffusion produces carburization within the grains with appreciable surface hardening. Mechanical property tests of Type

304 stainless steel which has been carburized in sodium within the volume diffusion temperature range (above 650°C) show increased strength and reduced ductility.

3. Nitrogen

Weeks and Klamut⁽²³⁾, in their discussion of liquid metal corrosion mechanisms, note that Gill and Bokros⁽¹³⁾ observed nitriding of Type 304 stainless steel due to migration of nitrogen in sodium at 540°C from a nitrogen cover gas. The nitriding observed was relatively rapid just below the sodium-nitrogen interface with the degree of nitriding decreasing with increasing distance from this interface. Brush⁽⁶⁾ has found that Type 347 stainless steel is readily nitrified in a 480-595°C sodium system having a nitrogen cover gas.

Mausteller⁽¹⁸⁾ reports the following results when nitriding was investigated in a number of sodium systems at temperatures up to 705°C:

- (a) With nitrogen cover gas, and no entrainment of nitrogen in the sodium, tool steel and stainless steels were unaffected.
- (b) The addition of one percent calcium to the sodium increased nitriding by acting as a nitrogen carrier.

Recent work⁽²⁶⁾ refers to oxidation studies in impure helium⁽²⁹⁾ which have revealed increasing oxidation rates with increasing thickness of nitride layers.

Weeks⁽²⁴⁾ reports on the effect of nitrogen in the alkali metals; noting that nitrogen like oxygen may have either of two effects. Nitrogen in solution in lithium is a much more active catalyst for corrosion than oxygen. Nitrogen may migrate through sodium from impurities in the cover gas to nitride steel, niobium, or zirconium surfaces. Calcium in sodium increases the nitrogen solubility and often introduces nitrogen and nitrogen transfer problems. This effect may override any benefit from the lowering of oxygen activity by calcium. This author notes that the large loop at Cadarache, France, has recently been shut down due to nitrogen embrittlement catalyzed by calcium in sodium.

Clark⁽⁹⁾ has reported a continuous build-up of nitrogen in the LAMPRE-1 sodium coolant system. The source of this nitrogen build-up was not located -- apparently it was not due to leaks in the system. Calculations indicated that the nitrogen might be entering the system by diffusion through the container walls.

4. Hydrogen

Sinizer and Pearson⁽²²⁾ note that there are no known effects of hydrogen in sodium on stainless steel core components. Weeks⁽²⁴⁾, however, reports that hydrogen embrittlement of the fuel elements occurred at temperatures less than 300°C in Dounreay from water in cover gas.

Hydrogen may react in conjunction with oxygen in accelerating corrosion of iron by sodium. National Research Laboratory work on iron solubilities in sodium showed approximately a ten-fold increase in iron solubility with the addition of oxygen and hydrogen (added as sodium hydroxide).

IV. CORROSION ASSOCIATED WITH ELEVATED TEMPERATURE

1. Intergranular Attack

Intergranular attack or "sensitization" has been discussed under the section dealing with carbon as an impurity and its mechanisms of attack.

2. Sigma Phase

Sigma phase is the formation of the intermetallic compound symbolized as Fe_mCr_n where m and n represent the proportions of iron and chromium in the structure. Theoretically m and n tend toward equality; however, sigma phase may vary over a wide range of compositions. It is usually found at the juncture of several grains rather than being generally distributed along the grain boundary as in the case for chromium carbide ($Cr_{23}C_6$) in sensitized steel. Mechanically, its effect on the steel is to greatly reduce ductility and impact resistance without giving rise to any visible external or surface attack. The detection of sigma phase is difficult since it forms over prolonged periods of exposure and apparently forms in a sporadic or inconsistent fashion.

Sigma phase formation has been reported in Type 316 stainless steel in sodium by Herzler and Young⁽¹⁵⁾. They observed one case which occurred in a hot rolled specimen exposed to 705°C sodium over approximately 4200 hours of exposure.

3. Mass Transfer

Mass transfer has been mentioned previously under oxygen attack where oxygen-catalyzed mass transfer is discussed as one of the mechanisms of oxygen attack, and under the section dealing with carbon as an impurity where carbon transfer results in decarburization and carburization reactions.

LaQue and Copson⁽¹⁷⁾ state that the 18-8 stainless steels are not susceptible to mass transfer up to 540°C, and the rate of transfer remains within tolerable levels up to 870°C. These authors also note that according to Hoffman and Manly⁽¹⁶⁾, the stainless steels and high-nickel alloys are probably the best available structural materials in dynamic sodium test systems, provided the hot-zone temperature of the system does not exceed 650°C and the temperature differential does not exceed 150°C.

Sinizer and Pearson⁽²²⁾ note that the transfer of metallic constituents such as Fe, Cr, Ni, and Mo have been studied; according to preliminary evidence, the effects of this transfer on the mechanical properties of stainless steels is minor compared to the potential effects of carbon transfer.

4. Stress

Stress as a promoter of carburization has been reported^(4,27). In this instance, a stressed sample of Type 316 stainless steel, exposed to 650°C sodium containing 30 ppm oxygen, carburized to a depth of about six mils while an unstressed sample had a diffusion layer less than two mils thick. Data are shown in Table VI⁽⁴⁾ which demonstrate the effect of stress on the depth of diffusion and on the amount of carbon which diffused into a sample of Type 316 stainless steel.

Table VI

CARBON PROFILES OF TYPE 316 STAINLESS STEEL
EXPOSED TO SODIUM AT 650°C(a)

Sample No.	39(3DLX3)	99
Exposure time, hrs	2,489	4,000
Stress level, psi	18,500	0
Average carbon content, ppm		
0-2 mils	3,211	1,063
2-4 mils	1,516	491
4-6 mils	686	561
6-8 mils	806	471
As-received carbon content, ppm	458	458

(a) Oxygen content of the sodium during this experiment was 30 ppm.

V. CONCLUSIONS

Information from the literature demonstrates that the impurities in the circulating fluid and the temperature of operation are the major factors controlling corrosion in a circulating sodium or NaK heat transfer system. The impurities which have been found to exert the greatest influence are carbon, oxygen, and nitrogen. Oxygen, by itself, seems to be acceptable as long as the concentration remains below about 100 ppm. Commercial grades of sodium, however, contain dissolved carbon

(probably 50-60 ppm) and carburization and decarburization reactions appear to be increased by oxygen concentrations above 50 ppm. When nitrogen is the cover gas, nitriding of steels has been reported to occur at the liquid metal-cover gas interface. Corrosion of nitrided steel is apparently promoted by the presence of oxygen. Nitrogen build-up in cover gas systems has been observed where no source of the nitrogen was readily determinable.

Sensitization, sigma phase formation, and mass transfer are directly influenced by elevated temperature (above 550°C). Changes in metal structure -- sensitization and sigma phase formation -- have not been shown to result in failure in sodium or NaK systems, although the sensitized structure is known to be very susceptible to intergranular corrosion in the presence of aqueous media. Mass transfer can be minimized by proper design of the system, selection of construction materials, and use of a low temperature differential in the system, as well as control of impurities in the circulating fluid.

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